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Mobile Laboratory for On-Site Monitoring of Hazardous Waste Incinerators

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MOBILE LABORATORY FOR ON-SITE MONITORING OF HAZARDOUS WASTE INCINERATORS

by

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Abstract

The Environmental Protection Agency (EPA) has increasingly viewed incineration as an effective means of destroying hazardous waste. Incinerators are permitted via a detailed trial burn under the Resource Conservation and Recovery Act (RCRA) to burn hazardous waste. These incinerators are then operated using carbon monoxide (CO) and other process parameters established during the trial burn to determine compliance.

Because of the interest in monitoring the performance of the incinerator on a real-time basis and the need to characterize the emissions from a variety of incinerators, the EPA built a mobile laboratory for real-time and near real-time monitoring of a hazardous waste incinerator's emissions and operating parameters. The result, the Hazardous Air Pollutants Mobile Laboratory (HAPML), is equipped with monitors for on-line analysis of inorganic and organic stack gas emissions. Instrumentation includes a gas chromatograph and mass spectrometer (GC/MS).

This report will discuss the development of the laboratory, results from the first field test as well as other combustion sources, and future plans.

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15. SUPPLEMENTARY NOTES AEERL project officer is Sharon L. Nolen, Mail Drop 62B, 919/541-7607. (*) Although all three authors are with EPA, the work reported was performed by Acurex Corporation.

16. ABSTRACT The report discusses: the development of EPA's Hazardous Air Pollutants Mobile Laboratory (HAPML), equipped with monitors for on-line analysis of inorganic and organic stack gas emissions and instrumentation including a gas chromatograph and mass spectrometer (GC/MS); results from the first field test and other combustion sources; and plans for the future. The EPA has increasingly viewed incineration as an effective means of destroying hazardous waste. Incinerators are permitted--via a detailed trial burn under the Resource Conservation and Recovery Act--to burn hazardous waste. These incinerators are then operated using CO and other process parameters established during the trial burn to determine compliance. Because of the interest in monitoring the performance of incinerators on a real-time basis and the need to characterize emissions from a variety of incinerators, the EPA built the HAPML for real-time and near real-time monitoring of hazardous waste incinerator emissions and operating parameters.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Laboratories	Pollution Control	13B	14B
Monitors	Mobile Equipment	Stationary Sources	14G	15E
Incinerators	Carbon Monoxide	Hazardous Waste		07B
Emission	Flue Gases			21B
Wastes	Gas Chromatography			07D
Toxicity	Mass Spectroscopy		06T	

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INTRODUCTION

The Environmental Protection Agency's (EPA) view concerning the disposal of hazardous waste has changed radically during its history. The Agency has progressed from viewing land disposal as virtually the only means of discarding waste to the restrictions of land disposal found in the Hazardous and Solid Waste Amendments of 1984 (HSWA) (1). As a result of this change in perspective, hazardous waste incineration (HWI) has increasingly been perceived as an effective means of destroying certain types of hazardous waste.

The land-based incineration of hazardous waste is regulated by the Resource Conservation and Recovery Act of 1976 (RCRA I) and its 1984 reauthorization (RCRA II). Incinerators are permitted under RCRA by completing a trial burn using the types and levels of waste or an acceptable substitute to be burned in the unit and meeting certain requirements during the trial. The destruction and removal efficiency (DRE) of the principal organic hazardous constituents (POHCs) must be greater than 99.99%. Hydrochloric acid removal must be greater than 99% or the emission in weight less than 0.5 g/s (4lb/hr), and the maximum particulate level must not exceed 0.183 g/dscm (0.08 gr/dscf) at 12% carbon dioxide (CO_2) (2).

Operating parameters established and the carbon monoxide (CO) level observed during the trial burn, while the RCRA requirements were achieved, are used to determine compliance for future operation of the incinerator. The operating parameters include types of waste to be burned, feed rate,

and temperature. Although the CO level has been used as a type of performance indicator for an incinerator, it has been found to represent general trends in DRE without reflecting minor changes (3).

Although DREs are used to indicate the performance of an incinerator, they are calculated only during the trial burn. Obtaining the information to calculate DREs is time consuming, costly, and, at the present time, not possible on a continuous basis. DREs also have a fundamental limitation. They do not take into account the presence of products of incomplete combustion (PICs). The DRE will not truly reflect the destruction and removal efficiency of a POHC if the POHC is also formed in the combustion process. Furthermore, it is possible that a different POHC can be formed in the combustion process that is more dangerous than the materials being incinerated.

Because of the interest in determining the performance of an incinerator on a real-time basis and the need to characterize the emissions from a variety of incinerators, EPA initiated a project to build a mobile laboratory for continuous monitoring of emissions and operating parameters of hazardous waste incinerators. The objective of this project was to provide an integrated sampling and analytical package for evaluation and development of continuous and semi-continuous monitors for hazardous waste incinerators. The result of the project is the Hazardous Air Pollutants Mobile Laboratory (HAPML), designed to be easily transported for use by research projects at a variety of incinerators.

This report will discuss the development of the HAPML, its capabilities, data obtained while monitoring various combustion sources, and future plans.

CONCLUSIONS AND RECOMMENDATIONS

The results of the field test indicate that the HAPML can be transported to a remote site and produce quality continuous emission monitor (CEM) results. Several problems in the organic system were identified during the field test, and steps have been taken to correct these problems. Data from the additional combustion sources tested illustrate the capabilities of the organic system.

There is, without question, a need for real-time measurement capability for hazardous waste incinerators. There is also a need for a continuous indicator of incinerator performance. The HAPML provides a means of testing a number of incinerators and can be used to characterize the volatile organics and permanent gas emissions.

The present work with the mobile laboratory is focused on determining the feasibility of using the mass spectrometer (MS) as a continuous monitor. This work includes two parts. First, different chemical classes in several concentrations must be tested to ensure delivery of a representative organic sample through the sampling system to the analytical instrumentation. Once this has been successfully demonstrated, the second aspect of the work will investigate the use of the MS as a selective ion monitor for products of incomplete combustion (PICs).

Future plans for the HAPML include support to a major field research project to measure the total mass emissions from a hazardous waste incinerator, further work with the rotary kiln, and additional study with the China coal project.

DEVELOPMENT OF THE HAZARDOUS AIR POLLUTION MOBILE LABORATORY

The HAPML was constructed to serve as an integrated sampling and analytical package for use in hazardous waste incineration research. The HAPML utilizes extractive sampling technology, and all components are housed in a standard 8 m long, self-propelled van.

The laboratory contains continuous monitors for real-time analysis of CO, CO_2, NO_x, O_2, SO_2, and HCl. Organic analytical instrumentation includes a gas chromatograph (GC) equipped with a flame ionization detector (FID) and a mass spectrometer (MS). All measurement sensors and the principles on which they are based are listed in Table 1. The layout inside the van is shown in Figure 1.

The sampling system was designed to deliver a portion of the gaseous effluent in the stack to the HAPML while maintaining sample integrity. Major considerations in on-line analysis include the interferences caused by particulates and moisture and minimizing reactions and interactions in the sample line.

All particulates must be removed from the sample stream because of problems they may cause in the analytical instrumentation. They can result in plugging of the lines, damage to the optical system, or light scatter resulting in erroneous data. The HAPML uses a particulate removal system located 3 m from the stack sampling port. The particulate removal system is housed in a heated aluminum filter box and consists of a high surface area, low pressure drop, spun glass wool filter. Valves are also located in this box to allow calibration gases to be sent from the van,

TABLE 1

MEASUREMENT SENSOR SUMMARY

Parameter	Instrument/Model	Measurement Principle
O_2	MSA Model 802	Paramagnetic
CO	TECO Model 48	Gas filter correlation
CO_2	MSA Model 303	NDIR
SO_2[a]	TECO Model 40	Pulsed fluorescence
NO_x	TECO Model 10	Chemiluminescence
HCl[a,b]	TECO Model 15	Gas filter correlation
Volatile Organics	Hewlett Packard 5890A	Gas chromatograph (FID detector)
	Extranuclear EL 150 (with extended range)	Mass spectrometer
Pressure	Validyne DP15-22 Differential	Pressure transducer
Stack	Omega Type K Temperature	Thermocouple

(a) Requires the TECO 900 sample conditioner
(b) Acquired since first field test

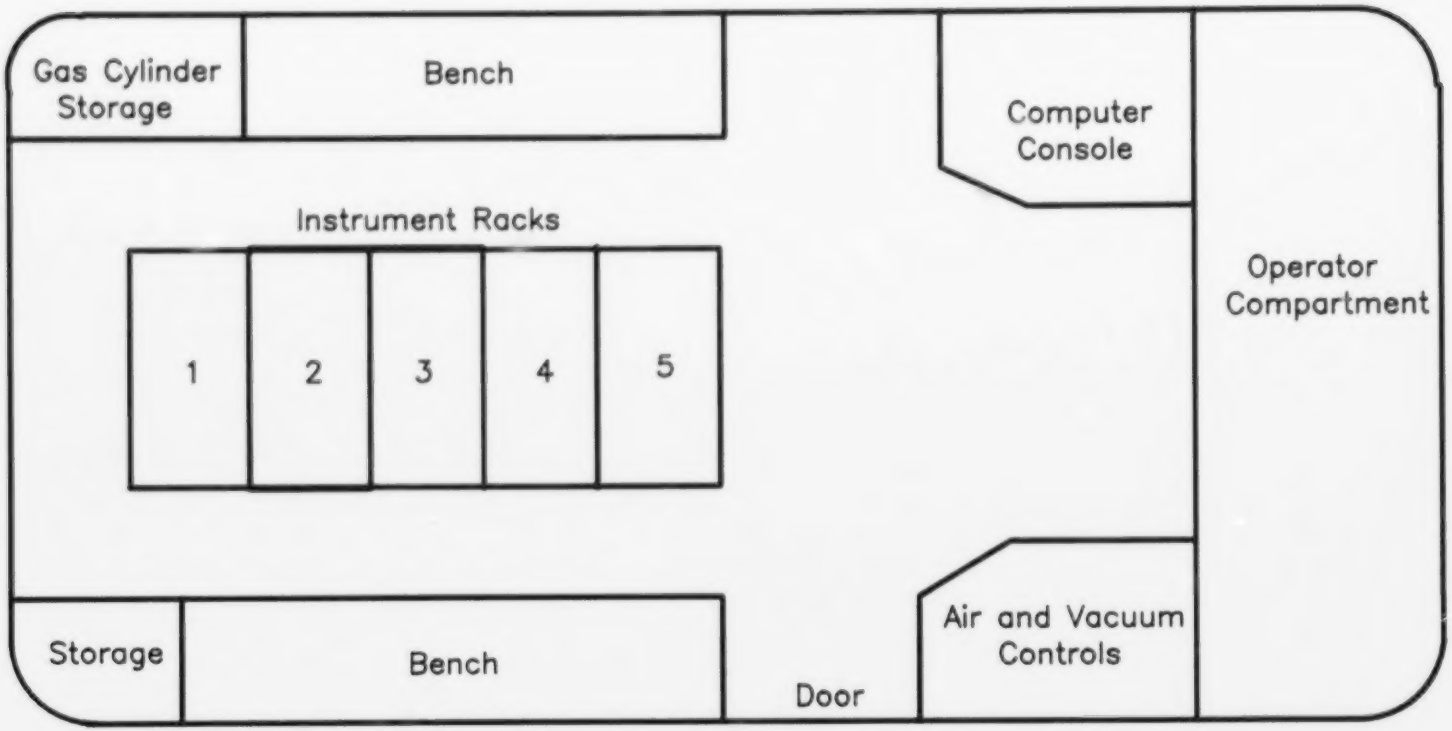


Figure 1. Floor plan of the Hazardous Air Pollutants Mobile Laboratory.

through the sampling system, back to the van, and into the appropriate analytical instrument for system checks.

Water, a natural combustion product, may condense within the analyzers or can result in optical interferences. This problem may be handled in different ways depending on the species of interest. The stack gas emissions flowing to the CO, CO_2, O_2, and NO_x monitors are cooled and dried using a condenser and a Perma-Pure dryer. Since SO_2 and HCl are soluble in water, these gases would be removed along with the water. Therefore, this problem must be resolved with a different procedure. A sample conditioner is used to dilute these gas streams with dry, clean air to minimize the interference effects of water vapor. NO_2 is also soluble in water. However, since NO_x is typically about 95% NO, the loss is considered negligible.

Several considerations are required to ensure that reactions in the sample line do not occur. A heated Teflon line is used to transport the sample from the stack into the mobile laboratory. The temperature of the sample line must be maintained above the boiling point of all compounds of interest. Care must be taken to eliminate any cool spots in the line, such as at fittings. If any chlorine is in the system, stainless steel connections can react with the sample and must be removed. Teflon fittings or stainless steel fittings lined with Teflon, which eliminate contact between the stainless steel and the sample, must be used.

The organic analytical system was designed to provide information in a variety of ways. The sampling system may be used to deliver sample gas directly to the GC/MS or the GC/FID for semi-continuous monitoring, to the MS for on-line analysis of selected organic compounds, or to the FID for total hydrocarbon (THC) concentration determination. It should be noted that the heated sample line transporting the stack effluent to the laboratory is heated to approximately 300°F (150°C). This limits the on-line organic analysis to those compounds with boiling points less than the temperature of the sample line. Many species of interest lie outside this range and may not be monitored in this fashion.

The HAPML may also be used as an on-site laboratory for analysis. It is equipped with a Volatile Organic Sampling Train (VOST) for collection and concentration of the gas effluent if the compounds of interest are present below the detection limits of the analytical instrumentation (4). These samples may be analyzed on the GC/MS or the GC/FID using a NuTech purge and trap system with a clamshell oven for thermal desorption. The purge and trap unit is equipped with a Tekmar sparger tube assembly. A quick analysis may be invaluable in determining the amount of stack gas to be concentrated to provide the proper amount of sample for more extensive analytical procedures. Also, organics collected on a sorbent material may be suspected of reacting, partially desorbing, or becoming contaminated if they are not stored properly or if they are not analyzed quickly enough. Therefore, analyzing the samples on-site improves the reliability of the results.

A two column option has recently been added to the GC to allow simultaneous operation of the GC/MS and the GC/FID. VOST samples may be analyzed on the GC/MS while the GC/FID is used for semi-continuous monitoring of selected compounds or vice versa. The only limitation is the temperature of the oven. It may be operated isothermally or, if a temperature program is used, the runs for the GC/FID and the GC/MS must be started simultaneously.

Standard gases traceable to the National Bureau of Standards (NBS) are used to calibrate the CEMs for quantitative analysis. Storage is available on-board for gas cylinders. A zero calibration (typically nitrogen gas) and standards in two concentrations are used each day of sampling to calibrate the instruments. The zero and the standard closest to the concentration seen while sampling are checked at midday and end-of-day. If analyzed concentrations of these gases fall outside specified limits, the instruments are recalibrated. The values from the calibration checks are used to determine the precision and accuracy of the instruments.

The organic system is calibrated in a similar manner, although the standards vary. When VOST analyses are being done, organic liquids are injected onto VOST cartridges, desorbed, and analyzed according to the VOST protocol. Standard gases for common organic classes are sometimes used as well as liquids injected directly into the GC. The HAPML is also equipped with a permeation chamber for calibration of the organic system and the HCl monitor. Most analysis done with the organic system is

qualitative and semi-quantitative. Precision and accuracy of the instruments are determined in a similar manner to the CEMs.

All MS and CEM data are acquired by two on-board computers (a DEC PDP 11 and a Compaq Deskpro 286). FID data are acquired using an HP3393A integrator. Backup of data collected is provided by strip chart recorders for the CEMs and a tape backup in the the Compaq computer.

FIELD TEST OF THE HAP MOBILE LABORATORY

The first field test of the HAPML was held in conjunction with a test of an industrial boiler. The complete boiler test was directed by Ivars J. Licis of EPA's Hazardous Waste Engineering Research Laboratory's (HWERL) Thermal Destruction Branch (TDB) in support of Marc Turgeon of EPA's Office of Solid Waste (OSW) to obtain more detailed environmental performance information that is reported separately. The field test was one of a series of tests to evaluate the feasibility of using industrial boilers to co-fire hazardous waste. Boilers, currently exempt from RCRA, are widely used in industry as an economical means of destroying on-site hazardous waste.

EPA's first tests found these boilers to produce high DREs (composite weighted DRE of 99.998%) under steady state operating conditions (5). Further tests were then initiated to examine performance of several types of boilers under transient and off-design operating conditions. The field test of the HAPML was held at one of these boilers.

The HAPML had several objectives during the field test. First, it was necessary to evaluate the performance of the mobile laboratory under field conditions. The data obtained with it were to be compared with the

data from the on-site instrumentation. Second, the mobile facility was to provide support to the HWERL/OSW effort by providing backups for the continuous monitors and additional organic capabilities. Third, the HAPML was to evaluate the feasibility of using combustion efficiency (CE) as an indication of incinerator performance.

The required performance level of CE is governed by international agreement for at-sea incineration; however, no criteria have been set for land-based incinerators. The CE is calculated from the CO_2 and CO data generated by two common continuous emission monitors (CEMs):

$$CE = \frac{CO_2 - CO}{CO_2} \times 100$$

where CO_2 and CO refer to the concentration of CO_2 and CO present, respectively. Under the international agreement, CE may not be less than 99.95% $\pm$ 0.05%. During the field test, CE data were to be acquired and compared to the DRE values for the same time period to determine if a correlation exists.

FIELD TEST RESULTS

The concentrations of the O_2, CO_2, and CO in the stack gas (along with the CE calculated from those concentrations and the DRE obtained) are shown in Table 2 for seven test conditions. The corresponding test conditions are listed in Table 3. The gas concentrations were acquired in 5 minute averages. The data presented in Table 4 demonstrate that the difference between the on-site and HAPML CEMs is within the precision of the instrumentation. The CE was calculated from each 5 minute average,

TABLE 2

TEST RESULTS OBTAINED FROM AN INDUSTRIAL BOILER CO-FIRING HAZARDOUS WASTE

Test No.	N[a]	O_2 Mean (%)	O_2 SD[b]	CO_2 Mean (%)	CO_2 SD	CO Mean (ppm)	CO SD	CE Mean (%)	CE SD	DRE (%)
7	18	7.67	0.59	11.13	0.24	22	0.87	99.98	0.0008	99.99991[c]
12	39	7.97	0.95	10.53	0.67	22	3.22	99.98	0.0045	99.9995
13	25	10.49	0.32	8.24	0.59	30	5.63	99.96	0.0079	99.9997
14	12	7.96	0.39	10.62	0.27	24	5.39	99.98	0.0053	100.0000
15	30	5.81	0.50	11.61	0.26	16	2.43	99.99	0.0018	99.9998
16	28	9.70	0.38	9.72	0.36	31	25.87	99.97	0.0262	99.9996
17	43	5.52	0.26	12.24	0.22	23	0.87	99.98	0.0008	(d)

(a) N=Number of data points
(b) SD=Standard deviation
(c) Only one DRE was obtained from each test
(d) No POHC burned in this test

TABLE 3

TEST CONDITIONS DURING THE FIRST FIELD TEST OF THE HAPML

Test No.	Condition
7	High load[a], coal, sludge, and TCB[b]
12	Low load, coal, oil, and TCB
13	Low load, high air, coal, oil, and TCB
14	Low load, coal, oil, and TCE[c]
15	High load, coal, oil, TCB, and metals
16	Low load, high air, coal, sludge, TCB, and metals
17	High load, baseline, coal, and sludge

(a) Load refers to steam
(b) Trichlorobenzene
(c) Trichloroethylene

TABLE 4

COMPARISON OF HAPML AND ON-SITE CEM DATA
AT FIRST FIELD TEST OF HAPML

	O_2 (%)	CO_2 (%)	CO (ppm)
Instrument Precision	±0.50	±0.15	±10
HAPML Average	7.65	10.70	24
On-Site Average	7.97	10.64	35

while the DRE was determined once for each test condition. The DREs were determined by Acurex Corporation, Mountain View, CA. The inlet concentration of the POHCs ranged from 5 to 10%.

Although differences were apparent between tests, an analysis of variance (ANOVA) was performed on the first four variables to confirm that there were statistical differences between the tests to allow for valid conclusions. Statistical differences were found at the $p = 0.0001$ level for all variables. A p-value of 0.05 or less is generally regarded as significant and 0.01 or less as highly significant. It was not unexpected to find a significant difference as the runs included baseline data. Separate ANOVAs were also performed on selected pairs of tests with the results discussed below.

Both tests 12 and 13 were burning coal, oil, and trichlorobenzene (TCB) at a low steam load. The only difference between the two tests was the difference in the amount of excess air. The typical level of excess air resulted in an oxygen level of about 7% in the stack. The high level of excess air used produced oxygen levels of 12 to 17%. All four variables in the two tests were found to be statistically different at the $p = 0.0001$ level. The CEMs reflect the differences between the test conditions. Test 13, with excess air, shows lower levels of CO_2 and CE and higher levels of O_2 and CO. The increase in CO and corresponding decrease in CE are probably due to the extra nitrogen in the air being heated and exhausted. This extra mass of air also shortens the residence time in the combustion chamber. The excess air may serve to quench the

reaction, causing the effect mentioned. The increase in the CO level with increasing O_2 (i. e., excess air level) is noted for all tests and is shown in Figure 2.

Another pair of tests, 12 and 14, were also compared. The two tests were identical except for the organic material being burned. (The POHC burned in Test 12 was TCB while Test 14 burned trichloroethylene (TCE).) There was no statistical difference between the two tests for any of the four variables.

As mentioned earlier, the primary purpose of this field test was to examine the feasibility of using industrial boilers for the destruction of hazardous waste under non-steady state conditions. In this particular case, boiler test loads and excess air levels covered the range used by the plant. For all tests, the minimum DRE was greater than the compliance level for hazardous waste incineration of 99.99% (6). Also for all tests, the CE never went below the minimum of 99.90% required for at-sea incineration. Figure 3 shows that all data points are well within the compliance window as defined by the CE and DRE limits.

The relationship between the accepted DRE surrogate, CO, and DRE has been explored (3). It was found that the CO level represents general trends in DRE without reflecting minor changes. The relationship between CO and CE seems to be similar to the relationship between CO and DRE.

It appears that CE may be a promising alternative to CO as an indicator of incinerator performance on a real-time basis. Like CO, CE is easily monitored and is relatively inexpensive to obtain continuously.

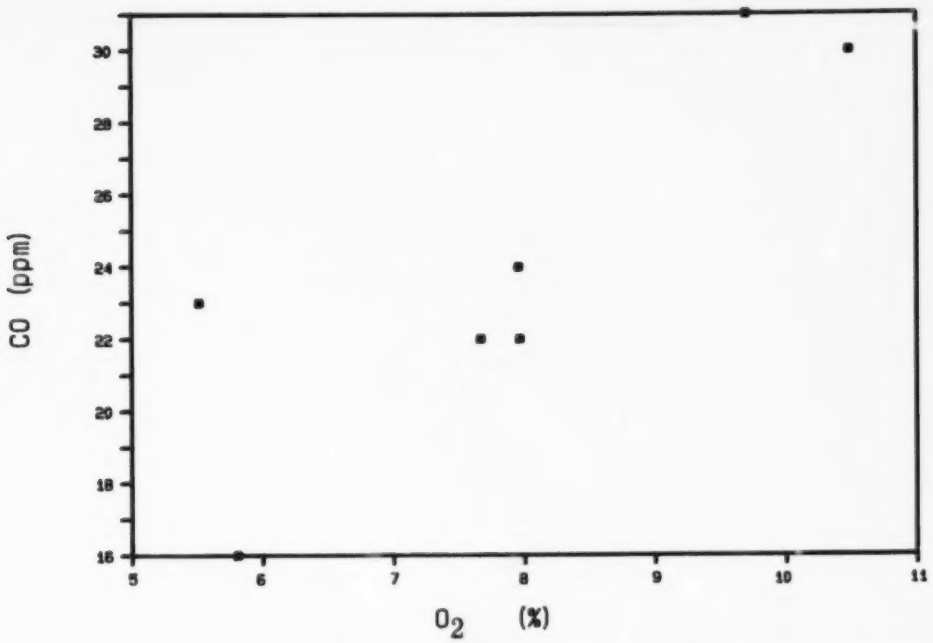


Figure 2. Comparison of CO and O_2 collected at a field test of an industrial boiler co-firing hazardous waste.

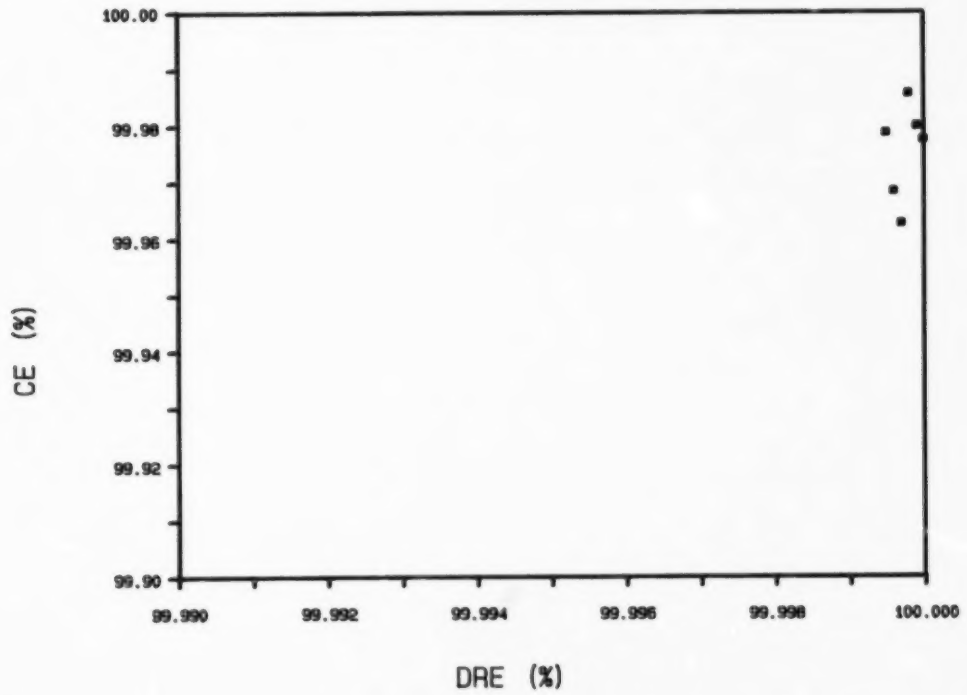


Figure 3. Comparison of CE and DRE shown in the "compliance window," collected at a field test of an industrial boiler co-firing hazardous waste.

However, the data generated in this work are limited. As illustrated in Figure 3, all points are at the upper end of the compliance window for both CE and DRE. To more fully determine the relationship between CE and DRE, further tests are required while an incinerator is operating under upset conditions and producing DREs over a greater range including ones less than the compliance minimum.

ADDITIONAL WORK

Following the field test, the HAPML participated in several local research efforts. The range of combustion sources demonstrates the versatility of the laboratory. Several of these projects and their results are discussed briefly.

The capabilities of the HAPML are illustrated by the data presented from EPA/AEERL's rotary kiln and woodstove studies. Figure 4 shows the rapid changes in the O_2 and CO_2 concentrations seen during the incineration of polyethylene bottles in the rotary kiln. This is due to the batch feed method used in the process. In contrast, the continuous monitor data from the woodstove stack shown in Figure 5 are much more stable as would be expected in steady state combustion.

It should be noted that the CEMs located with the kiln detected the same kind of peaks in concentration as the instruments in the HAPML. However, the peaks from the kiln CEMs were taller and sharper (7), indicating diffusion and mixing in the HAPML sample before it was analyzed. This is probably due to the long 200 ft (61 m) sample line used with the HAPML. In comparison, the sample line from the kiln to its CEMs is only

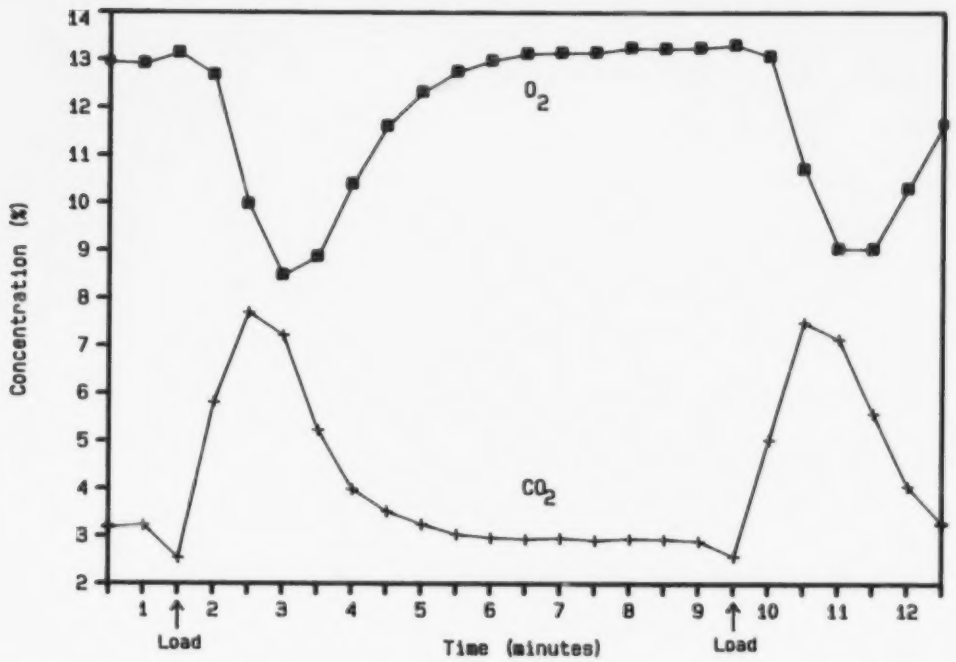


Figure 4. CO_2 and O_2 concentrations from the incineration of polyethylene bottles in the rotary kiln.

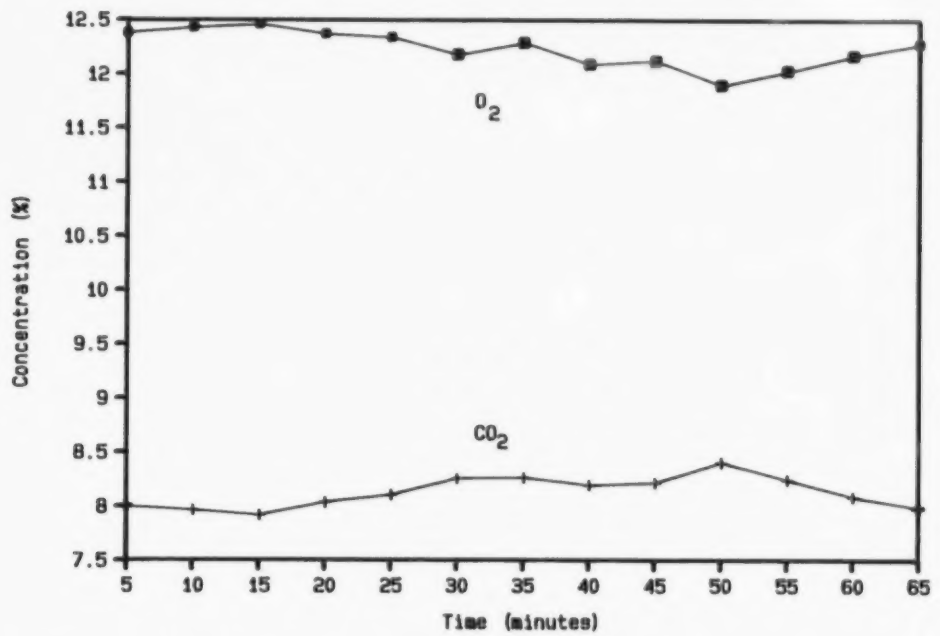


Figure 5. CO_2 and O_2 concentrations from woodstove combustion.

20 ft (6.1 m). Although the longer sample line may be required in some industrial locations, a shorter sample line has been procured for use when the greater length is not needed.

The CO_2 and O_2 levels seen from the combustion of wood are typical for a moderate burn rate. The burn rate and wood charged were done in accordance with the proposed NSPS method (8).

Organic stack emissions, PICs, from both the rotary kiln and wood-stove studies were collected by the VOST and analyzed on the GC/MS. GC/MS scan and relative concentrations of the compounds identified are shown in Figures 6 and 7. The aromatic PICs from the kiln reflect the conjugated bonds found in polyethylene. The PICs from the combustion of wood indicate the higher oxygen content of the cellulose.

The HAPML also participated in the China Coal Project. This effort is a long term epidemiological investigation of the marked increase in lung cancer incidence within a rural county in the People's Republic of China (PRC). Initial data have suggested that one of the fuels used by the residents for heating and cooking correlates with elevated lung cancer in both male and female members of the family (9). Samples obtained in China were analyzed for particulate and semi-volatile organic material, but no volatile organics could be measured due to limited field support capabilities.

In order to investigate volatile organic emissions and conduct more detailed testing of fuel impact, a simulated rural Chinese home was built including the open pit used to burn the fuels. Samples of two Chinese

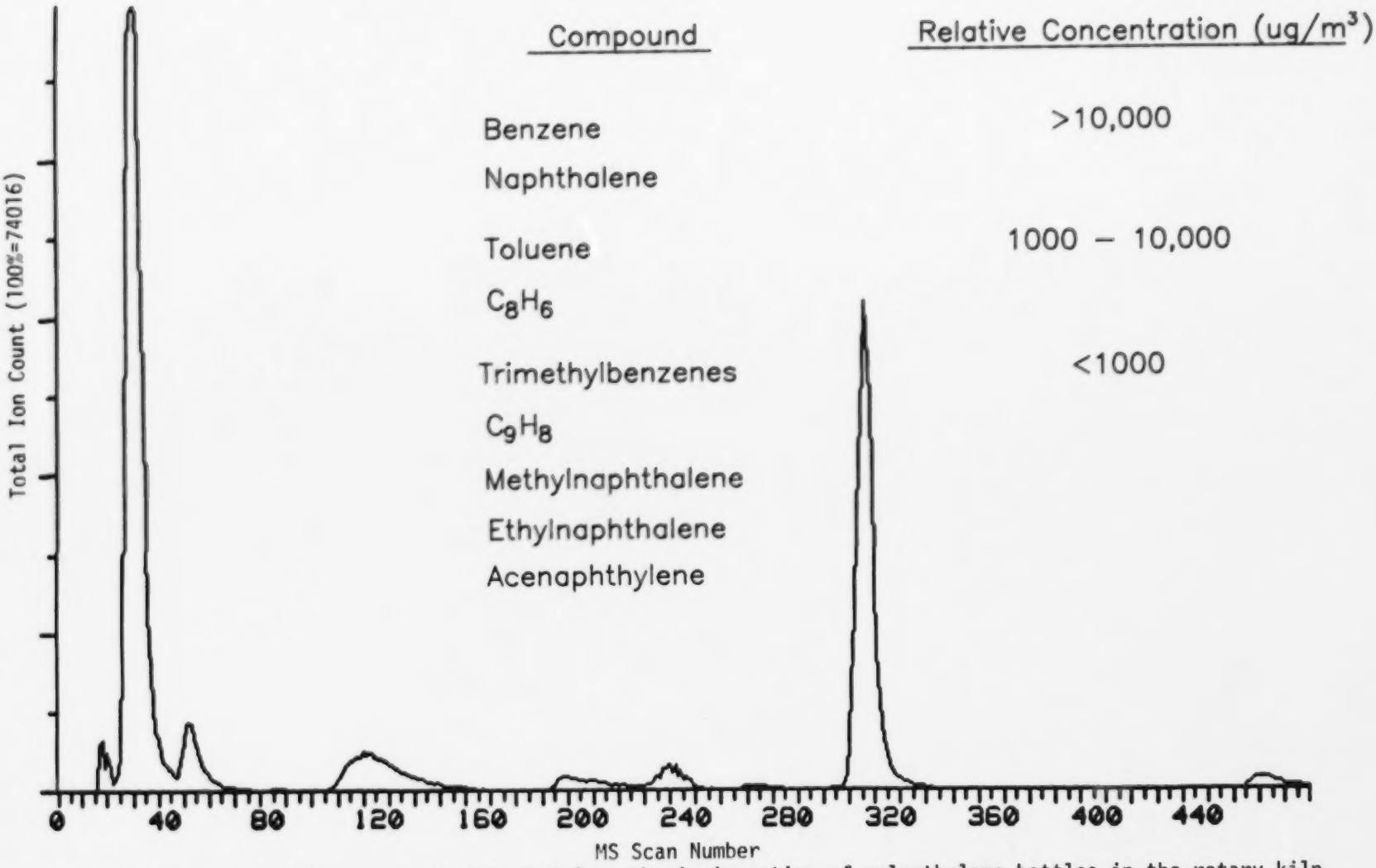
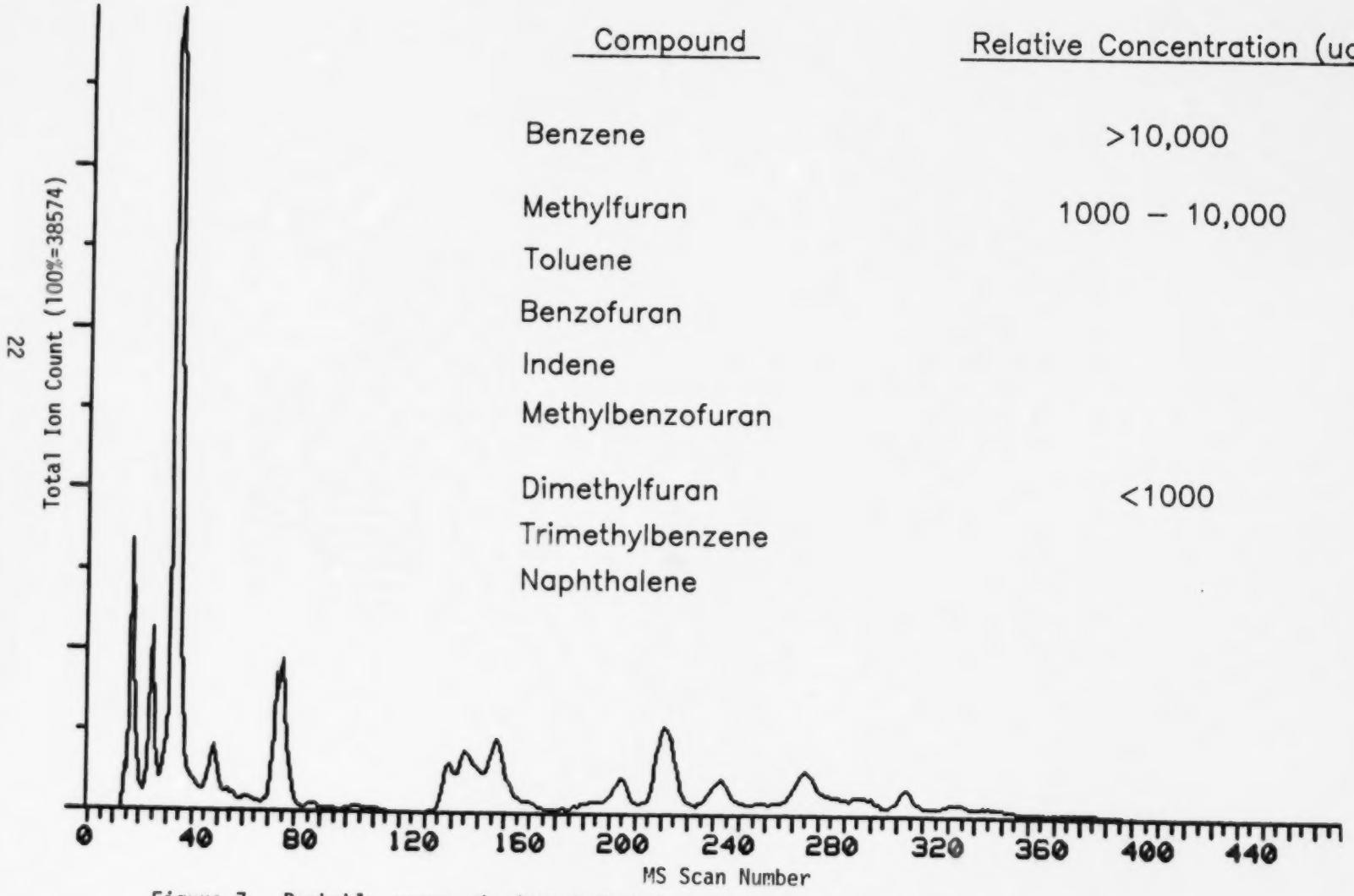


Figure 6. Probable compounds detected from the incineration of polyethylene bottles in the rotary kiln.



Compound	Relative Concentration (ug/m^3)
Benzene	>10,000
Methylfuran	1000 – 10,000
Toluene	
Benzofuran	
Indene	
Methylbenzofuran	
Dimethylfuran	<1000
Trimethylbenzene	
Naphthalene	

Figure 7. Probable compounds detected during woodstove combustion.

coals, one U. S. coal (Tennessee bituminous), and U. S. pine wood were burned in the manner used in the PRC (verified by visiting scientist from China). The same samplers used in China were used at this facility to establish similitude. The HAPML was added to the arsenal of analytical techniques to add data on the volatile emissions. Samples were extracted from the home at four different positions in the room simulating exposures when starting the fire, cooking, eating, and standing. Table 5 shows the dramatic variation found among the four fuels at the standing exposure level.

TABLE 5

CONCENTRATIONS OF SELECTED ORGANIC EMISSIONS
AT STANDING HEIGHT[a] IN SIMULATED CHINESE HOME

Probable Compound	Concentration ($\mu g/m^3$)			
	TN[b]	Smokeless[c]	Smokey[c]	U. S. Pine[d]
Benzene	1500	20	1000	500
Toluene	800	30	900	300
Naphthalene	1000	<10	400	200

(a) 1.6 m off the floor
(b) TN bituminous coal
(c) China Coal
(d) Wood

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APPENDIX

Quality Control Evaluation Report

The quality assurance project plan (QAPP) with revisions, which were submitted and approved, was followed. All revisions are on file with EPA/AEERL's Quality Assurance Officer.

The CEMs and the organic instrumentation were calibrated according to the QAPP and are described in the text. The GC/MS was tuned using perfluorotributylamine (PFTBA) as specified.

Field notebooks were kept by both van operators to record problems with instruments, maintenance, and field events that might affect the data acquired at that time.

Unfortunately, due to the operator problems experienced during the field test, data were not acquired for calculation of precision, accuracy, and completeness. Likewise, they were not calculated for the additional work due to the nature of that work. The purpose of the additional work was to investigate the possibility of using the HAPML for various combustion sources and were purely research/feasibility type studies.

The problems that have been experienced with QA have been addressed and corrected. For example, worksheets have been developed to ensure that the proper data will be recorded in the correct form. All QA procedures and revisions resulting from these studies have been incorporated into an improved QAPP for future work with the HAPML.

"QA/QC requirements are applicable to this project. The data contained in this report are supported by QA/QC documentation; however, the quality of the data produced did not satisfy the project level Data Quality Objectives. Therefore, there are limitations on the possible end uses of the data."